

# DEVELOPMENT OF POROUS CARBON MATERIALS FOR HIGH PERFORMANCE ELECTROCHEMICAL DOUBLE LAYER CAPACITORS

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## Introduction

Electrochemical double layer capacitors (EDLC) are electronic components, which store energy in the electric double layer by charge accumulation at the interface between the electrode and the electrolyte. These devices have wide applications as rechargeable energy storage systems and to avoid power interruptions. High energy and high power EDLC use activated carbons or glassy carbons as electrodes. Activated carbon is the material of choice in EDLCs because of its high surface area.

In general, it is believed that there is a direct relationship between the BET surface area and the double layer capacitance (DLC) of porous carbons [1,2]. However, a previous study has shown that, although surface area is very important, double layer capacitance is not always proportional to the BET surface area [3], but other properties as pore size distribution and surface chemistry also affect.

The first objective of the present work is to extend the study of EDLC to alkaline agent-activated carbons with highly surface area, which have hardly ever been studied, especially, in nonaqueous electrolyte. The second objective is to try to understand the relationship between carbon properties and capacitance. For this purpose, we have developed highly microporous activated carbons, by a simple preparation method, using KOH as activating agent, and activated carbon fibres (ACF), both with a wide range of surface area. The effect of the surface area and pore size distribution in DLC is analyzed.

## Experimental

Activated carbons have been prepared from two different precursors (an Spanish anthracite and a bituminous coal) using KOH as activating agent. The activation procedure is described elsewhere [4]. By changing the preparation conditions, activated carbons with different surface area (BET higher than 1400 m<sup>2</sup>/g) and pore size distribution have been prepared. In this study the nomenclature of the samples includes the activating agent (K), the carbonaceous precursor (UA, for the anthracite and HL for the bituminous coal), the KOH/coal ratio (31 for a 3/1 ratio), and the activation temperature (70 for 700 °C) and time. In addition, a commercial activated carbon (Maxsorb-

A) has also been studied. In the preparation of activated carbon fibers (ACF), Novolac-type phenolic resin was used as carbon precursor. The resin was spun to prepare the resin fiber. After stabilization of the resin fiber, it was activated in steam at 800 °C for different activation times. Surface area characterization of all samples has been carried out by physical adsorption (N<sub>2</sub> at 77 K and CO<sub>2</sub> at 273 K) using an automatic adsorption system (Autosorb-6, Quantachrome). For measuring the electric double layer capacitance, composite pellets electrodes have been prepared from powder activated carbon, acetylene black (Denki Kagaku Kogyo, Co. Japan) and binder (PTFE 6J, Du Pont-Mitsui Fluorochemicals Co., Ltd., Japan), in a ratio of 86:10:4 wt%, respectively. The composite electrode has been put on titanium mesh as current collector. The standard three-electrode cell has been utilized to measure the electric double layer capacitance of a single activated carbon electrode. Propylene carbonate containing 1.0 mol/dm<sup>3</sup> LiClO<sub>4</sub> electrolyte (1.0 M LiClO<sub>4</sub>/PC) has been used as nonaqueous electrolyte. The specific gravimetric electric double layer capacitance of the activated carbons has been calculated by the amount of electricity passed during positive process as described in the literature [5]. It has been used the galvanostatic method (40 mA/g) and a potential range from 2V~4V vs Li/Li<sup>+</sup>.

## Results and discussion

Figures 1 and 2 present the N<sub>2</sub> adsorption isotherms at 77K for the activated carbons and the activated carbon fibers, respectively. All of the samples present Type I isotherm, according to the IUPAC classification, characteristic of microporous solids. However, the shape of the isotherm for the sample KUA31951 is quite different to the rest. This shape is a consequence of the presence of mesopores (which is confirmed by the existence of a hysteresis cycle in the adsorption/desorption process). This sample has been prepared to study the influence of the mesoporosity in the EDLC. It can be observed that this series of activated carbons and ACF covers a wide range of surface area (BET surface area from 650 m<sup>2</sup>/g to 3500 m<sup>2</sup>/g) and pore size distribution (see the different knee of the isotherms).

Figure 3 shows the relationship between the BET surface area and the electric double layer capacitance (potential range 2V~4V vs Li/Li<sup>+</sup>) in 1.0 LiClO<sub>4</sub>/PC. This plot shows that a general trend between capacitance and BET surface

area exists for all the samples, although it is not a perfect linear relationship. These results indicate that although the BET surface area is a very important parameter, the EDLC seems to depend also on other characteristics of the porous carbon materials.

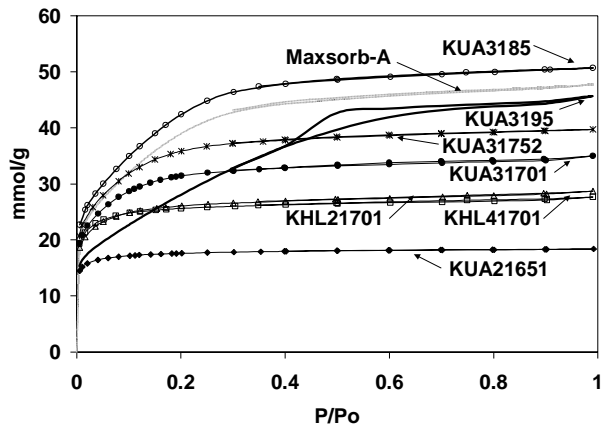


Figure 1.- N<sub>2</sub> adsorption isotherms at 77 K for the activated carbons.

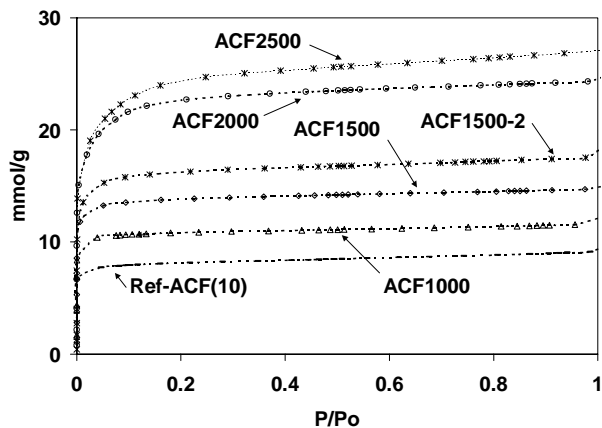


Figure 2.- N<sub>2</sub> adsorption isotherms at 77 K for the activated carbon fibers.

In Figure 3, the low range of BET surface area (< 2000 m<sup>2</sup>/g) corresponds to the series of ACF, which have EDLC values up to around 120 F/g. It can be seen that the ACF with the lowest surface area has a very low capacitance value. This must be due to the difficulty in forming effective double layer or low mobility of the electrolyte ions in the narrow micropores.

On the other hand, the high range of BET surface area (from 2000 to 3500 m<sup>2</sup>/g) correspond to the highly microporous activated carbons. It can be observed that these porous carbons, prepared in our laboratory, present high EDLC values, almost double that the ACF, reaching a value of 220 F/g. This value is similar to that obtained with a commercial activated carbon with one of the highest

surface area. These results are very interesting, taking into account the high values of the EDLC and that there are not many reports for the DLC of highly microporous activated carbons prepared using alkaline agents, especially in nonaqueous electrolyte such as propylene carbonate solution. It must be mentioned that the samples KUA31701, HL547IK and HL527IWK have higher EDLC values than the predicted from the general trend. This may be related to the narrow micropore size distribution or/and the difference in the surface chemistry.

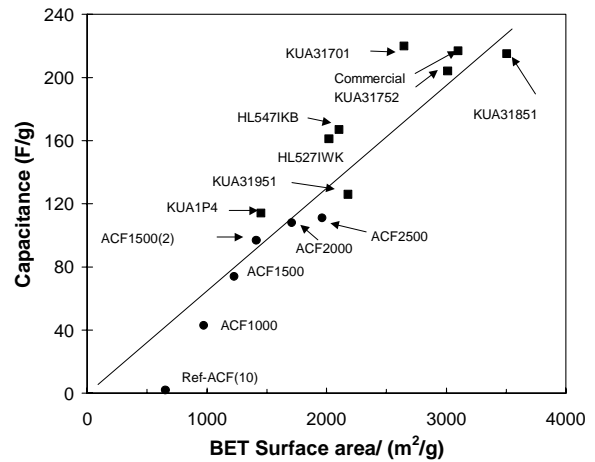


Figure 3.- Relationship between BET surface area and electric double layer capacitance (positive process) for all the samples in this study.

In a previous study [5], it was shown that, in activated carbons with surface area below 1500 m<sup>2</sup>/g, the presence of many mesopores is beneficial for the DLC. In order to study the effect of the mesoporosity in activated carbons with higher surface area, the capacitance of the sample KUA31951 has been measured. In Figure 3 it can be observed that, contrary to what was expected, the EDLC value for this sample is not very high (considering its surface area). This result seems to indicate that the presence of mesopores in activated carbons with very high surface area (> 2000 m<sup>2</sup>/g) is not very effective for the DLC, because these materials are composed of wide micropores that do not prevent the penetration of the electrolyte of EDLC into the pores.

## Conclusions

Highly microporous activated carbons with gravimetric-capacitance values in nonaqueous electrolyte as high as 220 F/g have been developed. Measurements of the EDLC of porous carbons materials with very different BET surface area (from 650 m<sup>2</sup>/g to 3500 m<sup>2</sup>/g) have shown that a relationship between the EDLC and BET surface area exist. In general, the higher the surface area the higher the capacitance. However, some samples deviates from that

trend, possibly due to the effect of the pore size distribution or/and the surface chemistry to the EDLC. In addition, it has been also seen that the presence of mesopores in activated carbons with very high surface area seems not to be important for the DLC.

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### **References**

- [1] Morimoto T, Hiratsuka K, Sanada Y, Kurihara K. *Journal Power Sources* 1996; 60:239
- [2] Lin C, Ritter JA, Popov BN. *Extended Abstract Carbon Conference 1997*; p.160.
- [3] Shiraishi S, Kurihara H, Tsubota H, Oya A, Soneda Y, Yamada Y. *Electrochemical and Solid-State Letters* 2001; 4(1):A5-A8.
- [4] Lozano-Castelló D, Lillo-Ródenas MA, Cazorla-Amorós D, Linares-Solano A. *Carbon* 2001.
- [5] Shiraishi S, Kurihara H, Oya A. *Carbon Science* 2001;1(3&4):133-137.